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INVESTIGATIONS OF THE BEHAVIOUR OF PERCHLOROETHYLENE AND SOURCE OF TRACE ORGANICS IN THE ST. CLAIR RIVER

by

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ABSTRACT

Observations of the movement and behaviour of perchloroethylene in flowing water in the presence of sand waves were made. The rate of dissolution of the perchloroethylene was also measured.

The annual loading of trace organics from municipal sources in the Sarnia area into the St. Clair River was also investigated.

MANAGEMENT PERSPECTIVE

The behaviour of perchloroethylene puddles resting on a transporting sand bed in flowing water has been clarified. The pore pressure to cause perchlorethylene to enter the sand layer was measured.

Results obtained enable improved interpretation of the impacts and behaviour of perchloroethylene released into rivers.

In addition, new data on the rate at which perchloroethylene will dissolve in running water is given which is significant for estimates of the fate of aromatic compounds.

Data specific to Sarnia is also provided for urban drainage containing various toxic substances and the rate at which near bank releases will dispense across the river. This information is significant for assessment of river quality and the contribution made to loadings by the urban area.

T. Milne Dick
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RÉSUMÉ

On a observé le mouvement et le comportement du perchloro-éthylène dans l'eau courante en présence de rides de fond. On a aussi mesuré le taux de dissolution du produit chimique en question.

On a effectué une enquête sur la charge annuelle de composés organiques à l'état de trace qui étaient déversés dans la rivière St-Clair à partir de sources municipales dans la région de Sarnia.

PERSPECTIVE-GESTION

On a tiré au clair la question du comportement des nappes de perchloro-éthylène retrouvées sur le fond de sable d'un cours d'eau courante. On a mesuré la pression d'eau interstitielle qui contraint le produit chimique à pénétrer la couche sablonneuse.

Grâce aux résultats ainsi obtenus, on a pu faire une meilleure interprétation des répercussions et du comportement du produit chimique déversé dans les cours d'eau.

De plus, on a recueilli de nouvelles données sur le taux auquel le perchloro-éthylène se dissoudra dans l'eau courante, lesquelles permettent de prédire la destinée des composés aromatiques.

On a fourni des données se rapportant précisément au réseau d'égouts urbain de Sarnia, lesquels renferment diverses substances toxiques et au taux auquel les émissaires à proximité des rives déverseront ces substances dans le cours d'eau. Ces renseignements sont très importants pour évaluer la qualité de l'eau de cette rivière et l'apport des charges de la zone urbaine avoisinante.

Le chef,

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Division de l'hydraulique

1.0 INTRODUCTION

As part of the effort by the National Water Research Institute to investigate the source of the tarry substances found on the bottom of the St. Clair River, some studies were carried out by the Hydraulics Division. These included observations of the movement of perchloroethylene (PERC) and its dissolution rate in the laboratory, calculations of the sediment transport capacity and properties of sand waves, calculations of dispersion from point sources and evaluation of trace organics in the urban runoff. These investigations and the results are presented in this report.

2.0 IN STREAM BEHAVIOUR OF PERC

2.1 Movement Over Sand Bottom

Very little is known about the physical behaviour of perchloroethylene in flowing water. The movement and transport of PERC, especially in the presence of bottom sediments, has not been studied. Therefore, some exploratory tests were conducted in a laboratory flume to gain insight into the behaviour of such material in the river and to help interpret some of the observations made in the field.

The tests were conducted in a flume 1 m long and 20 cm wide. The flume walls were made of glass. Water was fed from the head tank into the flume and the downstream level was controlled with a tailgate. The water depth was maintained at approximately 10 cm for all the tests.

Two different sizes of sand with mean diameter of 1.2 mm and 0.5 mm, respectively, were used as bed material in the flume. However, essentially the same behaviour was observed regardless of which size was used.

At the start of test, water was introduced into the flume and the discharge was slowly increased. A quantity of PERC, dyed to make it more visible, was introduced onto the top of the sand bed by means of a hypodermic needle. It was observed that small quantities of PERC released into the flow would form small globules of up to about 3 mm in

diameter. Larger quantities would form elongated puddles on the sand, similar to puddles of mercury on glass.

As the discharge was increased so that the average flow velocity reached about 20 cm/s, the PERC globules and puddles moved downstream on top of the sand bed until they came to troughs or depressions in the sand, where they would collect and coalesce.

As the discharge was further increased, bed sediment started to move and sand waves began to form. Any PERC that was released onto the bed was swept over the crest of the sand waves and collected in the troughs. There the puddles oscillated and occasionally small globules would detach and be carried farther downstream. However, at no time did any of this material move into the sand. A most interesting phenomenon occurred when the sand waves moved downstream over the puddles. As illustrated in Figure 1, the advancing sand wave would gradually bury the puddle that was sitting in the trough. As most of the puddle became buried, the portions of the downstream front sometimes broke off and were carried downstream. Eventually the puddle became completely buried and no evidence of it could be seen from the top. Later the PERC globule would reappear on the upstream face of the sand wave as it passed. It appeared at this point as if the globules were rising out of the sand when in fact the PERC had remained practically stationary while the sand wave moved by. As the PERC reappeared, globules would detach. These would be carried downstream over the crest of the sand wave or would roll down the sloping face, in the upstream direction, and stop in the trough.

These observations were made with pure perchloroethylene. Subsequent observations using the tarry material retrieved from the St. Clair River revealed the same behaviour.

The above observations were recorded on videotape.

2.2 Percolation Through Sand Layer

A test was carried out in the flume to obtain a rough measure of the pressure head required for the PERC to be forced upward through a sand layer. The bottom of the flume was fitted with a trough, 5 cm x 5 cm x 15 cm long, which was filled with sand. The top of the sand was flush with the flume bottom. PERC was fed to the bottom of the sand layer via tubing connected to the bottom of the trough, as shown in Figure 2. A column of PERC was built up as it was added to the tubing. When a certain height of the column was reached, the pressure was sufficient to force the PERC upward through the pores in the sand layer and it oozed out into the flume. The observations indicated that a pressure equivalent to about 10 cm of water when applied to the PERC was sufficient to force it to move upward through the sand layer. It was also observed that the PERC moved through the sand without disturbing or displacing it.

2.3 Tests of Dissolution Rate

Information on how quickly PERC would be dissolved by the flow once it gets into the river is useful for many investigations. Therefore, some tests were conducted in the flume by filling a tray with PERC and then running a flow of water over it for a period of time. The tray covered the full width of the flume and was 21 cm long and the top of the tray was flush with a bed of gravel which covered the flume bottom. The level of the PERC in the tray was monitored using a point gauge and samples of the water discharging at the end of the flume were taken for analysis of PERC concentrations.

The tests were conducted using three different water temperatures and two different mean flow velocities at every temperature. Care was taken so that the maximum velocity used was below that at which PERC would be removed from the tray by the action of waves at the interface.

Even though the dissolution rate should theoretically increase with the flow velocity and the water temperature, the time constraint did not allow detailed investigations to be made.

The test data show that, within the range of velocities and temperatures tested (0.1 to 0.2 m/s; 10°C to 20°C), the average rate at which the PERC was dissolved was about 40 $g/h/m^2$ of surface area. Thus it appears that the amount of PERC which would have been dissolved from the puddles found in the St. Clair would not be very large, especially considering that the PERC might have been buried for considerable periods of time.

2.4 Sediment Transport Capacity and Sand Wave Characteristics

These calculations were made based on the river conditions in the area of interest rather than the average values for the whole river because of the smaller flow depth and probably smaller sediment size in the strip of the river 100 m or so wide along the shore.

The flow rate was assumed to vary from 5320 m^3/s to 6510 m^3/s. .The flow depths were assumed to be 6.0 m to 7.0 m, respectively, for these two discharges. The median sand size was assumed to vary from 0.5 mm to 1.0 mm.

The sediment transport rate, calculated from the Ackers-White transport equation, varied from 1.5 to 2.7 tonnes per day per metre of river width. The length of the sand waves was calculated to be of the order of 40 m and the amplitude of the sand waves would vary between 0.75 m and 2.2 m.

It should be noted that these calculations were based on equilibrium conditions of sediment supply and transport, i.e., assuming that there is enough sediment supply from Lake Huron to satisfy the sediment-carrying capacity of the river. If the supply is less than the carrying capacity, then it is likely that sand waves of smaller amplitude will be formed.

Based on the sediment transport rates mentioned above and the sand wave geometry, estimates of the velocities at which the sand waves progress downstream can be made. These calculations show that the sand waves move at very low speeds, advancing only 4 to 5 m a day. Therefore it would take a sand wave about ten days to move past a given point.

2.5 Dispersion from Point Sources

Material that is released in a river will disperse as it is transported downstream. To learn how chemicals that are released from outfalls or that leach into the river will spread, some calculations were made for the stretch of the St. Clair downstream from the CN tunnel, assuming the existence of point sources at several locations. These calculations were based on the stream tube model, as described in the mixing model RIVMIX. The flow parameters used were as follows:

Discharge	= 6510 m^3/s
Depth	= 10.2 m
Velocity	= 1.04 m/s
Slope	= 0.000 025
Dispersion Coefficient	= 0.255 m^2/s

The approximate boundaries of three different plumes are shown in Figure 3. In general, it can be seen that the spreading rates of the plumes in the St. Clair are fairly slow.

Material that is released from the bank just downstream from the CN tunnel will occupy a plume of only about 150 m wide at a point some 2.5 km downstream. Material introduced at the centre of the river will not reach the bank for a very long distance downstream.

2.6 Discussion

The calculations show that the rate of dispersion of material in this particular river reach is rather slow and that material released from the bank will stay close to the shoreline for quite some distance. Therefore it is reasonable to expect that the tarry substance which was found close to shore came from a source or sources in the vicinity of the shoreline.

The laboratory observations showed that small globules of PERC would be transported by the current until they came to depressions, where they would collect to form larger pools. Thus a continuing source of even small quantities of PERC can collect into easily detectable puddles. They can be covered by the moving sand waves for days before reappearing again. Portions of the uncovered puddles may be transported downstream while portions may collect and be covered by the next sand wave. In this manner, material from the same puddle may be spread over a considerable distance in the downstream direction.

3.0 MUNICIPAL SOURCES OF TRACE ORGANICS IN THE SARNIA AREA

The study of the various sources of trace organics which were detected in the tarry globules in the St. Clair River was divided among several government agencies. The Hydraulics Divison was requested to evaluate the municipal (non-industrial) sources which are comprised of the following:

a) Water Pollution Control Centre (WPCC) effluent
b) Sewered urban runoff
c) Drainage ditch flow

A brief discussion of the above sources and their annual loadings follows.

3.1 Water Pollution Control Centre Effluent

Generally, municipal sewage should be free of toxic industrial effluents as stipulated by sewerage ordinances. However, toxic contaminants may be found in sewage because of illicit discharges, accidental spills, and domestic use of some trace organics (e.g., pesticides and insecticides). Trace organics in municipal sewage pass, largely untreated, through the WPCC and are discharged into receiving waters. The occurrence of trace organics in municipal sewage is enhanced in industrial areas with a higher probability of illicit discharges and increased background concentrations caused by local air pollution.

In the study area, two WPC centres discharge their effluents into the St. Clair River. The first one serves Point Edward and the second one serves Sarnia (including the township). The average daily discharges from these two plants are estimated as $6 \times 10^3 m^3$/day and $56 \times 10^3 m^3$/day respectively. The combined annual discharge of primary effluent is estimated as $22.6 \times 10^6 m^3$/yr.

Limited samples of the Sarnia WPCC influent and effluent were collected and analyzed for selected trace organics. the full list of organics studied included 31 substances. Among these, six substances found in tarry globules were of particular interest. For that reason,, these six substances are discussed in more detail in this report. The information for the remaining 25 substances will become available later.

The following substances were selected for detailed study:

Perchloroethylene
Hexachloroethane (HCE)
Hexachlorobutadiene (HCBD)
Pentachlorobenzene (QCB)
Hexachlorobenzene (HCB)
Octachlorostyrene (CS)

Among the above substances, the first five are included on the US EPA list of priority toxic pollutants. The first one, perchloroethylene, was found in tarry globules in the highest quantity (about 45%) and served as a carrier for other toxic compounds. The remaining five compounds were selected by the NWRI study team as marker compounds suitable for tracing organics sources.

The levels of the selected six compounds in the WPCC effluent are listed in Table 1 and the calculated loadings are listed in Table 2. In this case, only liquid samples were collected. Since these samples were not filtered prior to the extraction, the reported values include some quantities extracted from suspended solids.

The levels of organics in the WPCC effluent are relatively low with a few exceptions. Among the flobule compounds, only perchloroethylene is found in greater quantities (26 ppb), though such levels are not unusual and do not pose a threat to the receiving water body. The annual loading for this substance was calculated as about 600 kg/yr.

Among other elevated levels (greater than ppb), one could name chloroform (2.2 ppb) and trichloroethylene (6 ppb). Neither of the above levels is excessive.

3.1 Urban Runoff

Urban runoff is recognized as a non-point sources of trace organics. Depending on the type of sewerage, runoff is discharged into receiving waters in the form of combined sewer overflows, stormwater discharges, or overland flow.

The origin and transport of trace organics in urban runoff were studied earlier in a number of Ontario municipalities. It appears from these studies that organics are transported by both water and solids suspended in runoff. The organics originate from both atmospheric and land-based sources. Atmospehric sources, which are particularly important for dissolved organic loadings, include both local and remote sources.

Suspended solids may transport trace organics in appreciable quantities, depending on the compound properties. This source of organics is closely related to local land-use activities.

A survey of the study area identified 12 outfalls which discharge runoff into the St. Clair River. These 12 outfalls comprise four combined sewer overflows, seven storm sewers and the municipal drainage ditch. Additional outfalls drain the adjacent industrial area (the chemical valley), but these private drainage systems were not accessible to the study team. For considerations of organic inputs to the St. Clair River, it is adequate to consider a single combined runoff discharge through all outfalls except the municipal ditch. The ditch receives some leachate and industrial discharges which alter dramatically the composition of its flow and it is therefore considered separately in the next Section.

Recognizing the effects of land use on runoff quality, it was desirable to subdivide the developed area into two sub-areas and to design the sampling program accordingly. The first sub-area (see Fig. 4) represents Point Edward and Sarnia (without the industrial part) and the second sub-area represents the chemical industry area northwest of Vidal Street S.

The non-industrial sub-area comprises about 21 km^2 of primarily residential urban land. To estimate the loading of trace organics in runoff from this area, it was necessary to calculate the annual runoff volume and to estimate its composition by sampling. The annual runoff volume was estimated by the Soil Conservation Service (SCS) method as $5.2 \times 10^6 m^3/yr$. An additional volume is discharged in the form of combined sewer overflows which were estimated as 5% of the annual sewage volume, or $1.1 \times 10^6 m^3/yr$. Thus the total annual volume of runoff and overflows from this sub-area is $6.3 \times 10^6 m^3/yr$. Using mean concentrations of suspended solids in this volume, the annual yield of suspended solids was estimated as 1100 tonnes/yr.

Samples of runoff and wet-weatherflows in combined sewers were collected at three sites listed in Table 1. The first site was a

combined sewer overflow structure at Clifford Street. The second site was located on Campbell Street, just east of Whitmore Avenue. Finally, the third site was located on Cathcart Blvd. east of Lecaron Avenue, fairly far from the industrial area.

Analytical results for water samples collected at the above three sites are given in Table 1 for compounds found in tarry globules. The results do not show much variation. The lowest levels were found at the combined sewer overflow where two thirds of data were below the detection limit.

The second sub-area was the industrial area at the south end of the City of Sarnia. This sub-area comprises 4 km^2 of industrial land enclosed by the St. Clair River, St. Clair Parkway, Vidal Street and Christina Street (see Fig. 4). Two sampling sites were established along the perimeter of the sub-area, on Vidal Street. The Vidal St. north site was established at the junction of Vidal and St. Andrew streets. The Vidal St. south site was established about 100 m north of Churchill Road. Since the whole area is served by private roads and sewers, it was not possible to establish other sites closer to the sewer outfalls.

The analytical results obtained for both industrial sites are shown in Table 1. Although the contaminant levels observed were somewhat higher than those in residential areas, the differences were not pronounced.

The annual runoff from the industrial sub-area was estimated as 1.7 x $10^6 m^3/yr$ and this volume is expected to carry about 700 tonnes of suspended solids.

Since the differences in the composition of residential and industrial runoff were relatively small, it was decided to combine both sub-areas in calculations of loadings. Thus, the combined area produces about 7.8 x $10^6 m^3/yr$ of runoff and about 1800 tonnes/yr of suspended solids. In loading calculatins, the maximum runoff concentrations from Table 1 were adopted to compensate for non-monitored inputs within the industrial area. The calculated loadings are given in Table 2.

Besides water samples, a number of sediment samples has been also collected. Only some of these samples have been processed so far. Analytical results given in Table 3 include data for three runoff sediment samples. The observed levels are relatively low. There was no need to consider these sediment data in loading calculations, because of the extractions of unfiltered water samples.

3.3 Municipal Drainage Ditch

The municipal drainage ditch was evaluated separately from other stormwater discharges. Although the ditch carries primarily surface runoff from an area of about 16 km^2 (measured upstream from the culvert at Vidal Street), it also receives numerous industrial discharges and possibly the leachate from the disposal facilities along Scott Road. It is therefore expected that the composition of the ditch flow is controlled by industrial effluents.

For the contributing area upstream of Vidal Street, the anual runoff was estimated by the SCS method as 2.5 x $10^6 m^3/yr$. The flow in the ditch was sampled at two points. The first sampling site was at the culvert on Scott Road, just downstream of waste disposal sites. The second sampling point was at the culvert on Vidal Street. It is recognized that downstream of this culvert, the ditch receives some additional discharges. Such discharges could not be evaluated because of the lack of information on drainage patterns and the lack of access for sampling.

The analytical results for the ditch samples are shown in Table 1. With the exception of perchloroethylene, the observed levels are significantly higher than those for any other sites. Using the data from Table 1, the annual loadings for the drainage flow were calculated and given in Table 2.

Two sediment samples were also collected in the municipal drainage ditch. The analytical results are given in Table 3 and

indicate fairly high levels (in ppm) which significantly exceeded the results reported earlier for other sites.

3.4 Comparison of Loadings from the Sources Studied

The annual loadings of six primary compounds were given in Table 2. These loadings were plotted in Fig. 5 for the sources studied - the WPCC effluent, urban runoff and the municipal drainage ditch. It appears from these data that the total annual loadings from all three sources are in most cases dominated by a single source. For three marker compounds with highest loadings, the predominant source is the municipal drainage ditch. For the carrier, perchloroethylene, the predominant source is the WPCC effluent. The last source produced the highest loading among all the substances studied - about 600 k/yr of perchloroethylene.

3.5 Conclusions

The surface runoff and the WPCC effluent from the Sarnia area $33 \times 10^6 m^3$ of flow to the St. Clair River. This volume is fairly well distributed during the year, with the annual peak discharge of about 40 m^3/s. The combined runoff and effluent flows carry about 4000 tonnes of suspended solids annually.

The flows from the various sources studied contained trace organics at relatively low levels. The most prevalent substance was perchloroethylene which is discharged in the WPCC effluent at a rate of about 600 kg/yr. The marker compounds found in tarry globules in the St. Clair River, such as HCE, HCBD, QCB, HCB and OCS, were found in much smaller quantities. Their annual loadings varied from 0.1 to 10 kg/yr. For most marker compounds, the annual loading was mostly contributed by the municipal drainage ditch. None of the observed trace organic levels was high enough to pose a threat to the receiving water body.

Considering the relatively large quantities of perchloroethylene and marker compounds found in the St. Clair River, the non-industrial municipal sources cannot be considered as significant sources of such compounds.

3.7 Acknowledgements

Analysis of all water and sediment samples were done by the Environmental Contaminants Divison (ECD) of NWRI The contribution of Dr. B. Oliver and ECD staff is gratefully acknowledged.

TABLE 1

Levels of Selected Trace Organics in Water Samples from Study Area

Compound	Water Sample Concentrations in µg/L (ppb)							
	WPCC Effluent	Urban Runoff					Municipal Ditch	
		Combined Sewer	Residential		Industrial			
			Campbell	Cathcart	Vidal N.	Vidal S.	Scott Rd.	Vidal St.
Perchloroethylene	26.0	.100	.050	.100	.050	.090	5.00	3.500
HCE	.002	ND	.001	.001	.003	.010	.420	.640
HCBD	.001	ND	.001	.009	.007	.008	.830	3.700
QCB	ND	ND	ND	.001	.002	.002	.015	.041
HCB	.003	.001	.005	.003	.010	.017	.018	.024
OCS	ND	ND	ND	.002	.002	.001	.012	.003

TABLE 2

Annual Loadings of Selected Trace Organics

Compound	Annual Loadings in kg/yr		
	WPCC Effluent	Urban Runoff	Municipal Drainage Ditch
Perchloroethylene	590.0	.78	8.8
HCE	.045	.078	1.6
HCBD	.023	.070	9.3
QCB	~.011	.016	.103
HCB	.068	.133	.060
OCS	~.011	.016	.008

TABLE 3

Levels of Selected Trace Organics in Sediment Samples

	Sediment Sample Concentrations in µg/kg (ppb)				
	Urban Runoff				Municipal Ditch
	Residential		Industrial		
	Combined Sewer	Cathcart	Vidal N.	Vidal S.	
Perchloroethylene	41	29	5.9	-	66
HCE	36	-	ND	ND	ND
HCBD	58	-	8	25	4300
QCB	ND	-	3.3	ND	490
HCB	710	-	32	160	1700
OCS	100	-	9.9	ND	1400

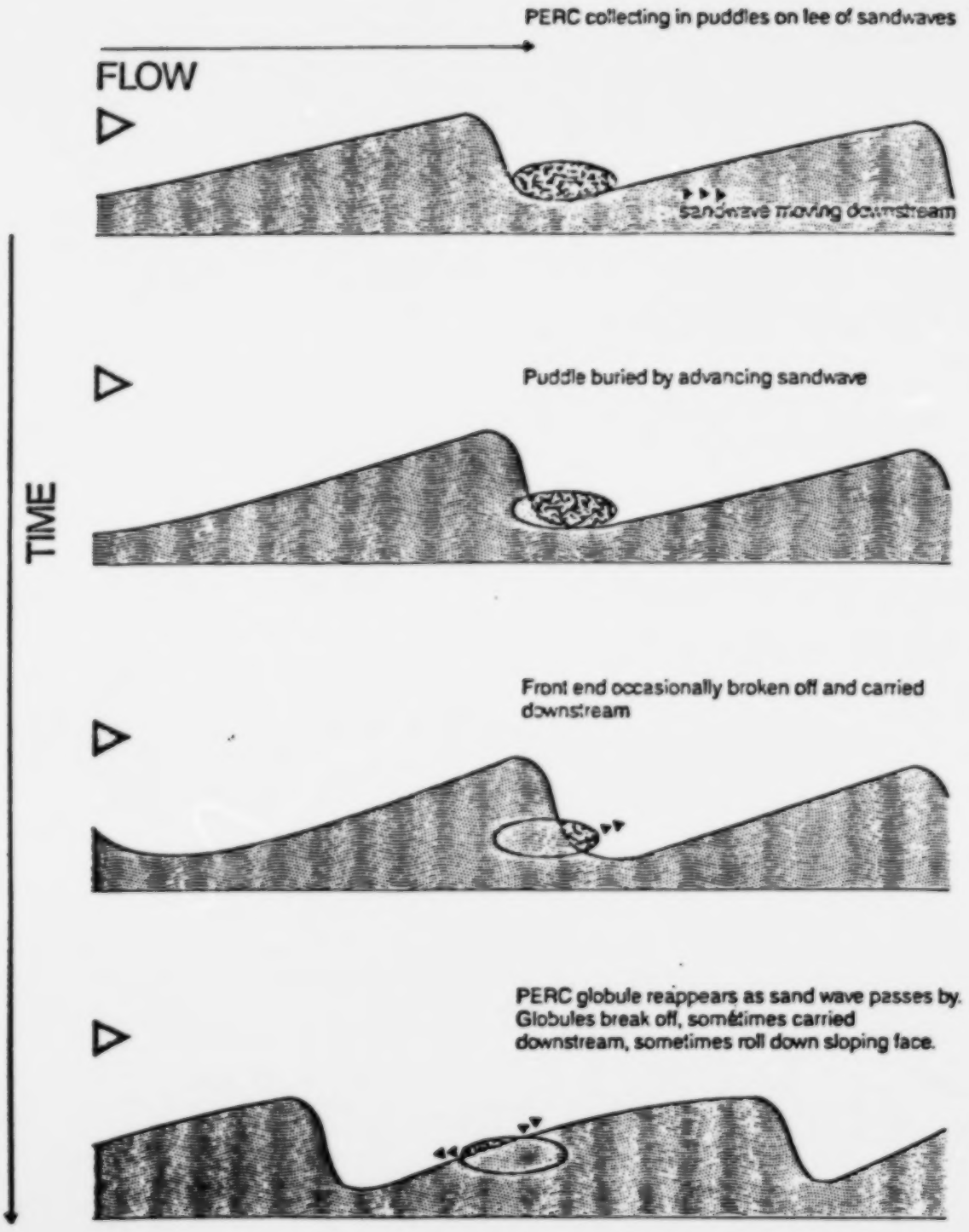

PERC collecting in puddles on lee of sandwaves
FLOW
Sandwave moving downstream
Puddle buried by advancing sandwave
TIME
Front end occasionally broken off and carried downstream
PERC globule reappears as sand wave passes by. Globules break off, sometimes carried downstream, sometimes roll down sloping face.

Figure 1. Movement of PERC in presence of sandwaves.

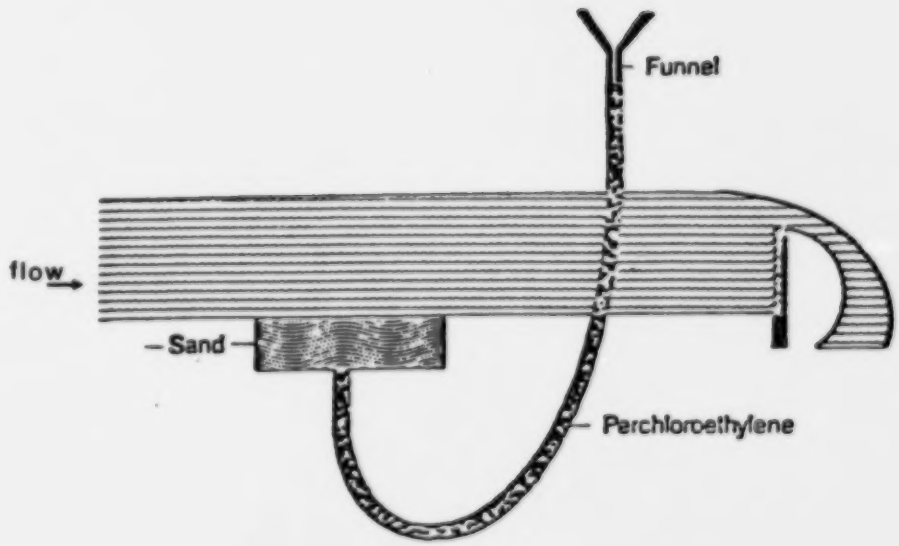


Figure 2. Equipment for observing percolation of PERC through sand.

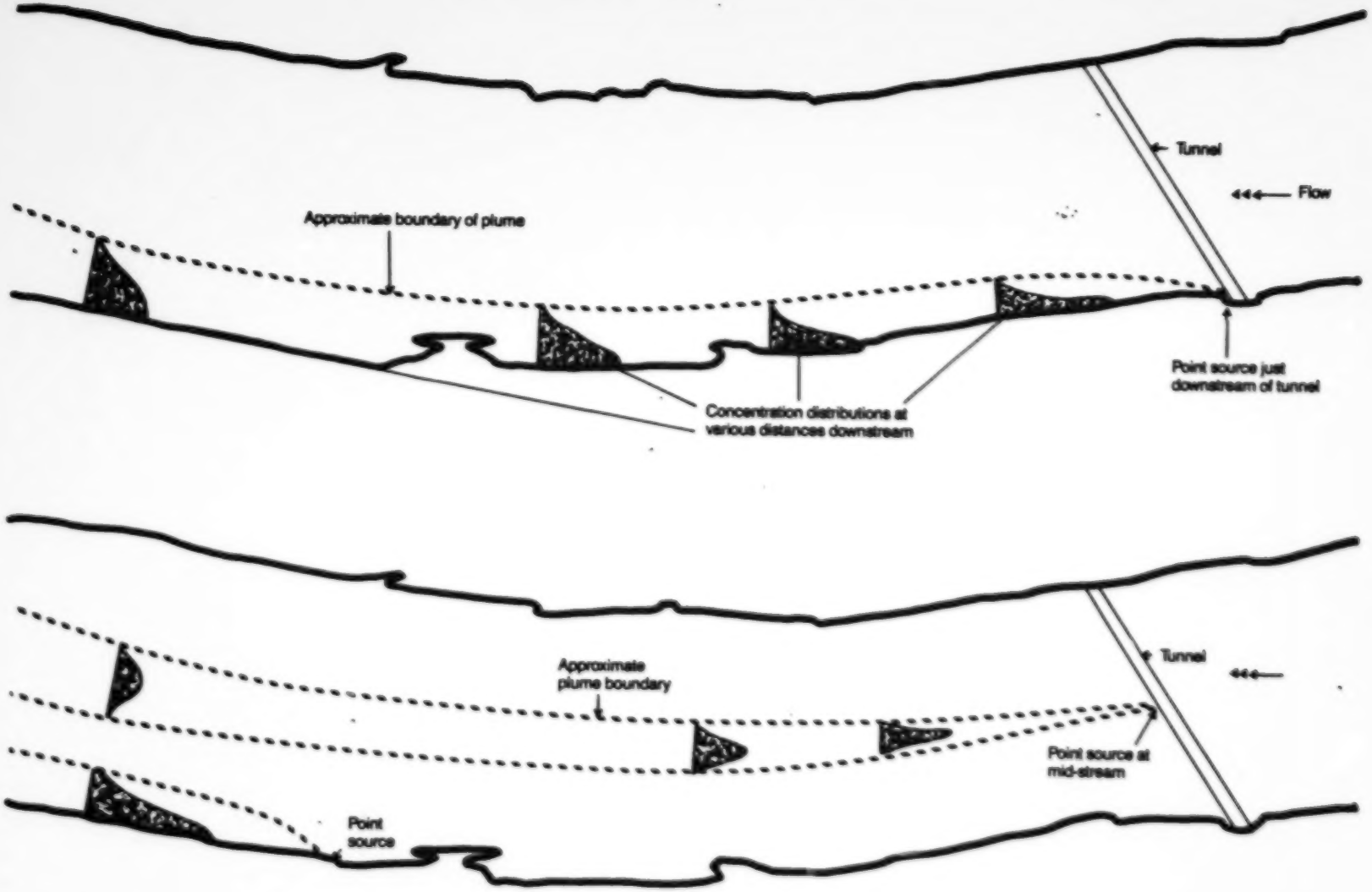
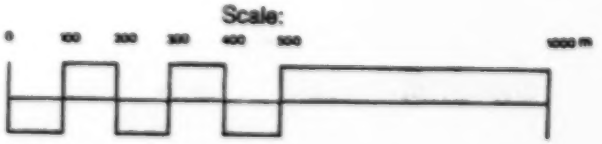


Figure 3. Plume boundaries and relative concentrations from several assumed point sources.



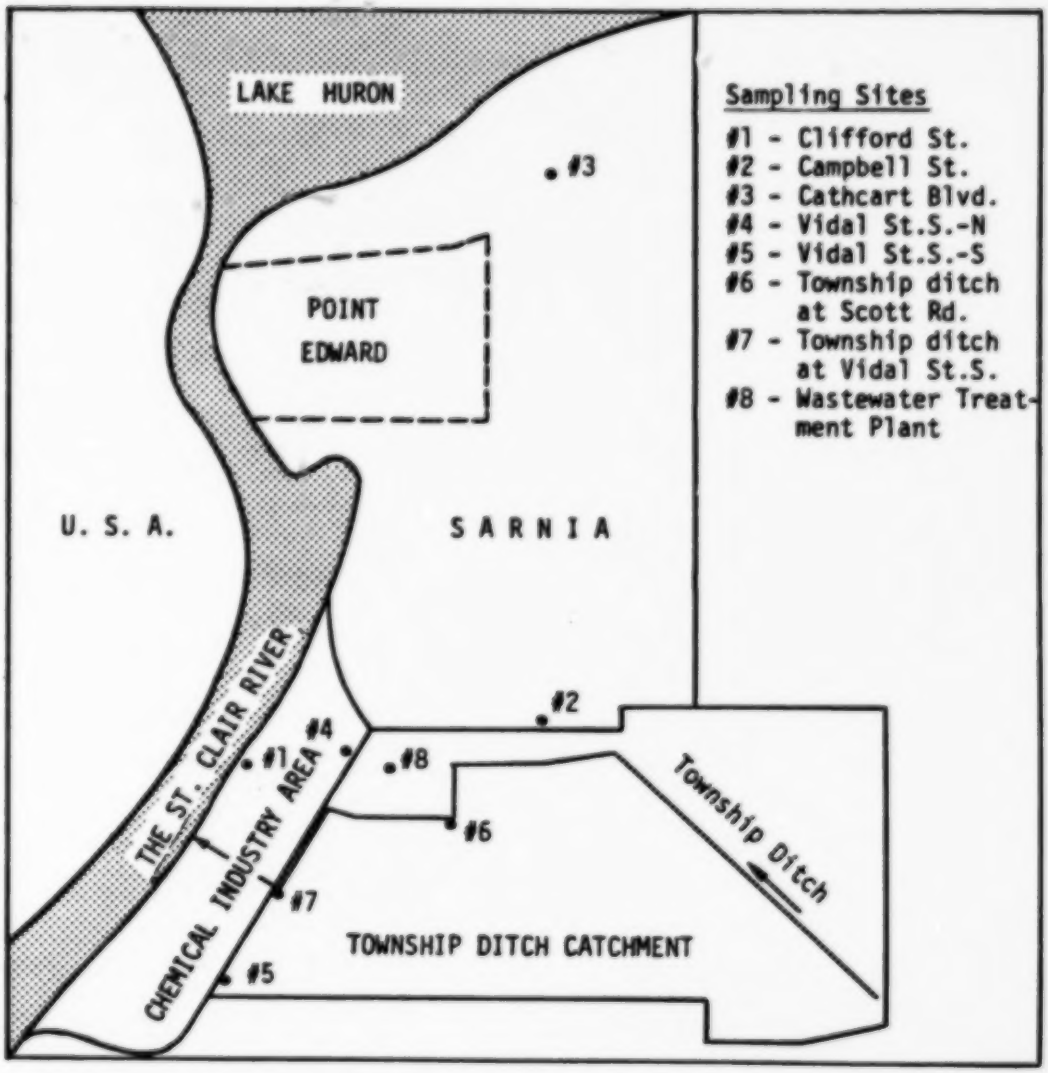


Figure 4. Location map

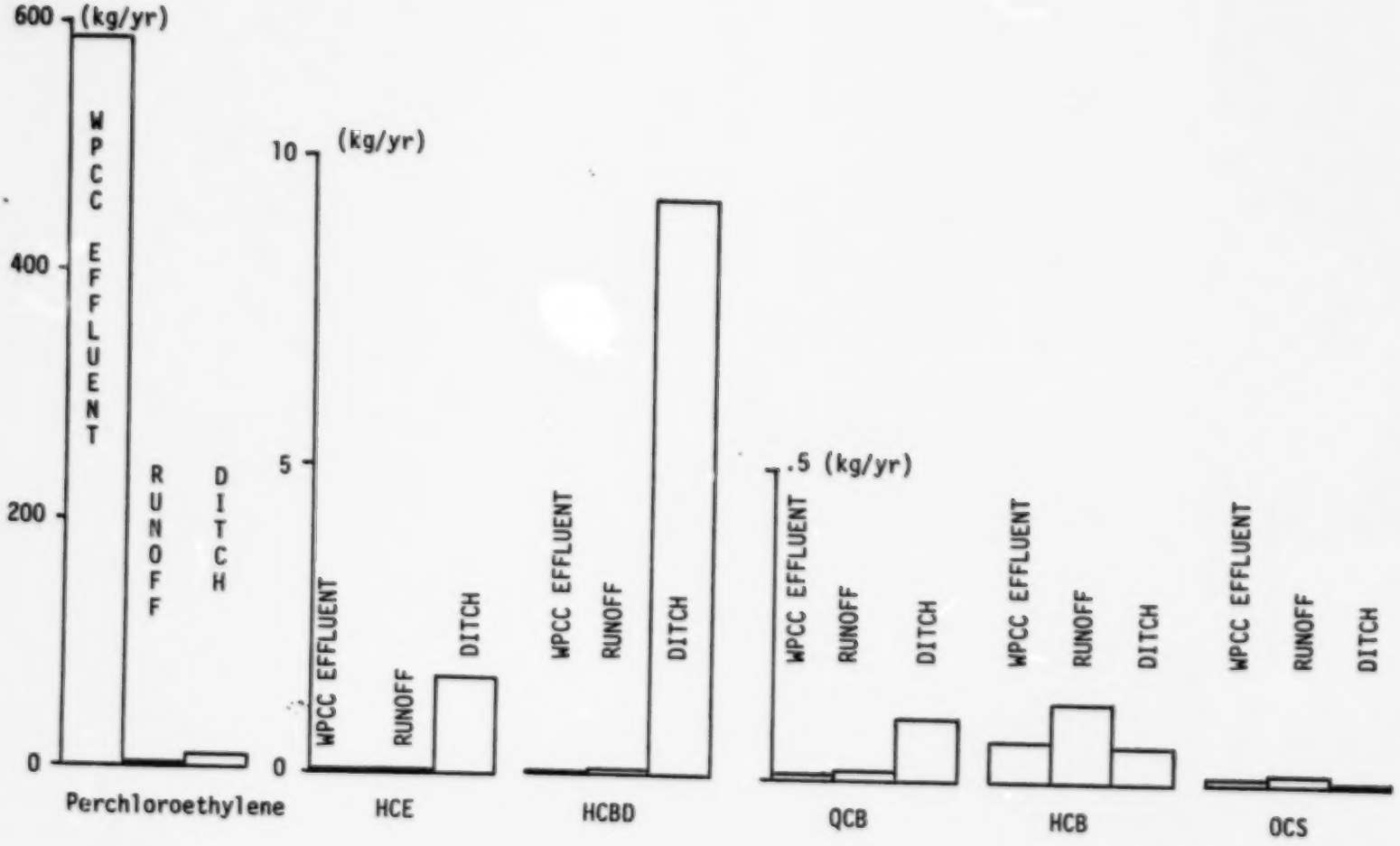


Figure 5. Annual loadings of selected compounds from three sources.